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Synthesis of an amphiphilic conjugated polymer through block copolymerization of phenylacetylene and (p-trityloxycarbonylphenyl)acetylene and the subsequent hydrolysis

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Summary

The polymerization of (*p*-trityloxycarbonylphenyl)acetylene (*p*-TrOCOPA) with $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ ternary catalyst proceeded in a living fashion to provide polymer with low polydispersity index (M_w/M_n ~1.1) in good yield. Block copolymerizations of *p*-TrOCOPA with phenylacetylene (PA) selectively formed the corresponding block copolymers regardless of the order of monomer addition. The hydrolysis of the homo- and block copolymers of *p*-TrOCOPA catalyzed by hydrochloric acid gave carboxyl-containing hydrophilic homopolymer and amphiphilic block copolymers, respectively. The amphiphilic block copolymer formed micelles in solution and monomolecular membrane at the air-water interface.

Introduction

It is known that rhodium complexes catalyze the polymerization of phenylacetylene (PA) to give poly(phenylacetylene) [poly(PA)] having cis-transoidal main chain [1]. Further, Noyori et al. have achieved the living polymerization of PA by using rhodium catalysts such as $(nbd)Rh(C{\equiv}CPh)(Ph_3P)_2$/DMAP [2] and $[(nbd)Rh(OMe)]_2/Ph_3P$/DMAP [3], (nbd: bicyclo[2.2.1]hepta-2,5-diene, DMAP: 4-(dimethylamino)pyridine). However, these catalyst systems require the addition of DMAP to prevent the formation of inactive binuclear complexes, and the initiation efficiencies are not quantitative [4]. Recently, we have reported that the $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ ternary catalyst induces living polymerization of PA. The initiation efficiency of this system is quantitative and end-functionalized polymers are easily prepared by use of (triphenylvinyl)lithiums having functional groups [5].

In principle, the synthesis of block copolymers is possible by sequential polymerization, if several monomers polymerize in a living fashion with the same catalyst. In a previous paper, we reported that $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ ternary catalyst induces living polymerization and block copolymerizations of various para-substituted PAs [6].

Amphiphilic polymers, which contain hydrophobic and hydrophilic moieties in one molecule, display surface activities such as ability to decrease the surface tension, and many studies have been carried out on their syntheses and properties [7]. However, there are few examples of the synthesis of amphiphilic polymers that contain conjugated main chain.

In this study, we examined the homo- and block copolymerizations of (*p*-trityloxycarbonylphenyl)acetylene (*p*-TrOCOPA), and further performed the hydrolysis of block copolymers to convert them into amphiphilic copolymers. PA and (*p*-methoxyphenyl)acetylene (*p*-MeOPA) were employed as comonomers.

Experimental

[(nbd)RhCl]$_2$ and triphenylphosphine were used as purchased. PA was distilled twice from CaH$_2$ at reduced pressure. Diethyl ether was distilled from sodium/benzophenone ketyl. Tetrahydrofuran (THF) was distilled from CaH$_2$ and further distilled from sodium/benzophenone ketyl. *p*-MeOPA and *p*-TrOCOPA were synthesized by applying the literature methods and purified by recrystallization [6,8]. Ether solution of (triphenylvinyl) lithium (50 mM) was prepared by the literature method [6].

Polymerizations were carried out under dry nitrogen in a Schlenk tube equipped with a three-way stopcock. A typical procedure was as follows: The catalyst solution was prepared by adding an ether solution of (triphenylvinyl)lithium (2.0 ml, 0.10 mmol) to a THF solution (3.0 ml) of [(nbd)RhCl$_2$ (12 mg, 0.025 mmol) and triphenylphosphine (39 mg, 0.15 mmol). After catalyst aging for 15 min, polymerization was initiated by adding a THF solution of monomer (0.125 M, 4.0 ml, 0.50 mmol) to 1.0 ml of the catalyst solution. Triethylamine was added in the polymerization of *p*-TrOCOPA to prevent the deactivation of the propagating species by the carboxyl group of (*p*-carboxyphenyl)acetylene, a remaining synthetic intermediate. The polymerization was allowed to proceed at 30 °C for 2 h. Resulting polymers were precipitated into a large amount of hexane (in the case where the formed polymers contain *p*-TrOCOPA units) or methanol (in the other cases), filtered, and dried in vacuo at room temperature. The molecular weights and polydispersity indices (PDIs) of polymers were determined by GPC (eluent THF, columns Shodex KF805L x3, polystyrene calibration).

Hydrolyses of the *p*-TrOCOPA units were carried out in methanol (20 ml) by stirring with aqueous acid solutions (2.0 N) of 1-10 equivalents to the ester group of polymers (*ca*. 0.5 mmol) at room temperature. After the reaction, polymer was reprecipitated into a large amount of diethyl ether, filtered, and dried in vacuo at room temperature. Molecular weights and PDIs were determined by GPC (eluent THF, polystyrene calibration) after conversion into the methyl ester derivative by using trimethylsilyldiazomethane [9]. The degree of hydrolysis and the block compositions of hydrolyzed block copolymers were determined from ^{1}H NMR spectra of hydrolyzed and esterified products in DMSO-d_6 and benzene-d_6, respectively.

Results and Discussion

Living polymerization of p-*TrOCOPA*

In order to confirm the living nature of polymerization of *p*-TrOCOPA with $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ ternary catalyst, multistage polymerization was examined. (Figure 1). The solid line in Figure 1 stands for the theoretical number-average molecular weight for the living polymerization with quantitative initiation. Polymer was obtained in virtually quantitative yield at every stage and the molecular weight of polymer increased in proportion to the polymer yield. The GPC traces of these polymers showed no shoulder, indicating that propagation species kept their activity even after the completion of polymerization. This result manifests that the present polymerization of *p*-TrOCOPA proceeds in a living fashion. Poly(*p*-TrOCOPA) was soluble in DMSO, DMF and THF and partly soluble in benzene and toluene.

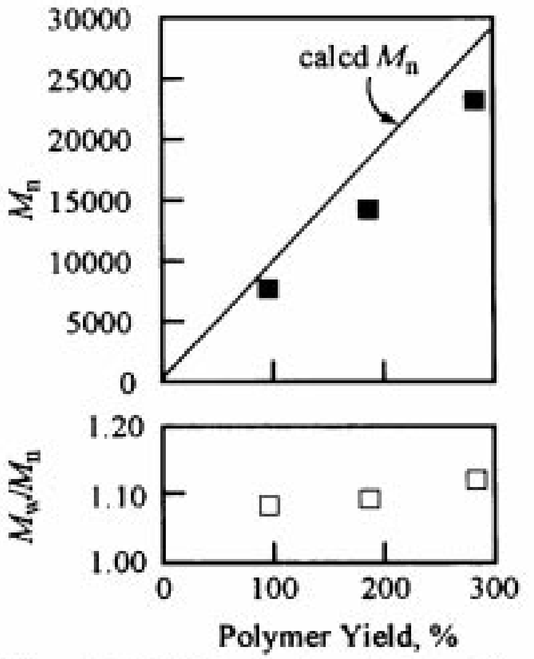


Figure 1. Multistage polymerization of *p*-TrOCOPA (in THF at 30 °C for 2 h for each stage; $[M]_{0,add}$ = 50 mM, $[[(nbd)RhCl]_2]$ = 1.0 mM, $[Ph_2C{=}C(Ph)Li]$ = 4.0 mM, $[Ph_3P]$ = 6.0 mM, $[p\text{-TrOCOPA}]_0/[Et_3N] = 4$).

Block copolymerization of p-TrOCOPA with various PAs

Since it was proved that *p*-TrOCOPA polymerizes in a living fashion, block copolymerization of *p*-TrOCOPA with either PA or *p*-MeOPA was examined. The results are shown in Table 1. The GPC traces of the block copolymers kept unimodal, and showed no shoulder irrespective of the order of monomer addition. The molecular weights of the block copolymers increased compared to those of the first-stage polymers, while the PDIs of the block copolymers remained as small as those of the first-stage polymers. These results verify that block copolymers have been selectively obtained.

Table 1. Block copolymerization of *p*-TrOCOPA with either PA or *p*-MeOPA[a)]

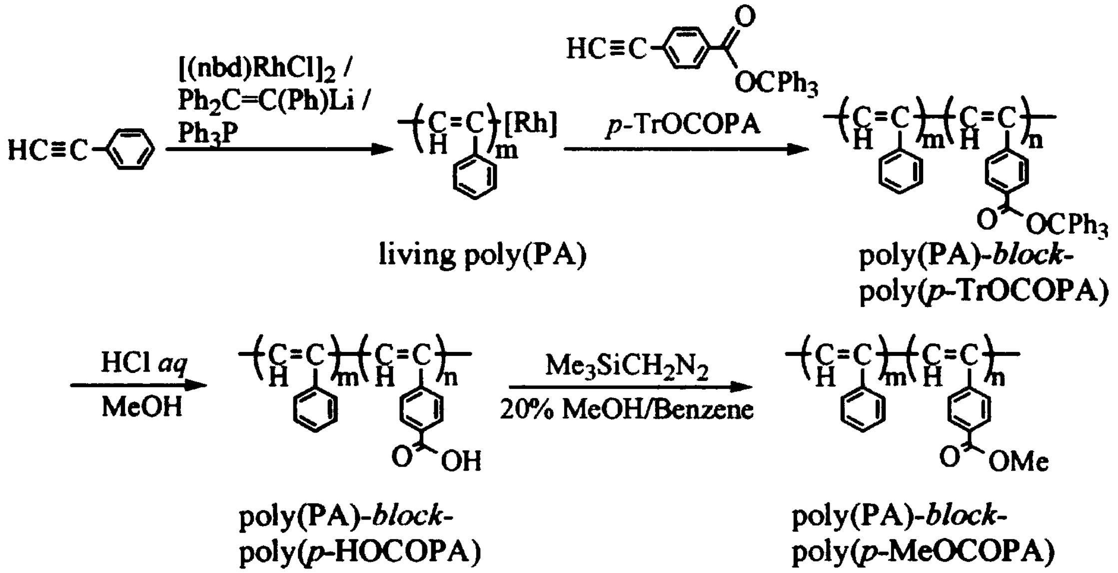
Run	Monomer		Polymer	
	M_1	M_2	M_n[b)]	M_w/M_n[b)]
1	*p*-MeOPA	–	7800	1.25
2	*p*-MeOPA	*p*-TrOCOPA	20500	1.23
3	PA	–	5700	1.19
4	PA	*p*-TrOCOPA	20000	1.18
5	*p*-TrOCOPA	–	14300	1.13
6	*p*-TrOCOPA	PA	21500	1.14
7	*p*-TrOCOPA	*p*-MeOPA	22200	1.17

a) Polymerized in THF at 30 °C for 2 h (for *p*-TrOCOPA) or 1 h (for other monomers); $[M_1] = [M_2] = 0.10$ M, $[[(nbd)RhCl]_2]$ = 1.0 mM, $[Ph_2C{=}C(Ph)Li]$ = 4.0 mM, $[Ph_3P]$ = 6.0 mM, $[p\text{-TrOCOPA}]_0/[Et_3N] = 4$).

b) Determined by GPC (THF eluent, PSt standard).

Hydrolysis of p-TrOCOPA-containing homo- and copolymers

Since block copolymerizations of *p*-TrOCOPA proceeded to give the corresponding block copolymers selectively, we then examined the conversion of trityloxycarbonyl group into carboxyl group by hydrolysis (Scheme 1). At first, hydrolysis of the homopolymer, poly(*p*-TrOCOPA), was examined in methanol at room temperature in the presence or absence of acids [8]. The results are shown in Table 2. We employed here the homopolymer whose number-average degree of polymerization (DP_n) was 75. When hydrochloric acid was used as catalyst, hydrolysis proceeded within 1 hour and a homogeneous orange solution was obtained. Consequently, 98% of the ester group was hydrolyzed, while the degree of polymerization of the resulting poly(*p*-



Scheme 1. Preparation of amphiphilic block copolymer, poly(PA)-*block*-poly(*p*-HOCOPA).

Table 2. Hydrolysis of poly(*p*-TrOCOPA)[a]

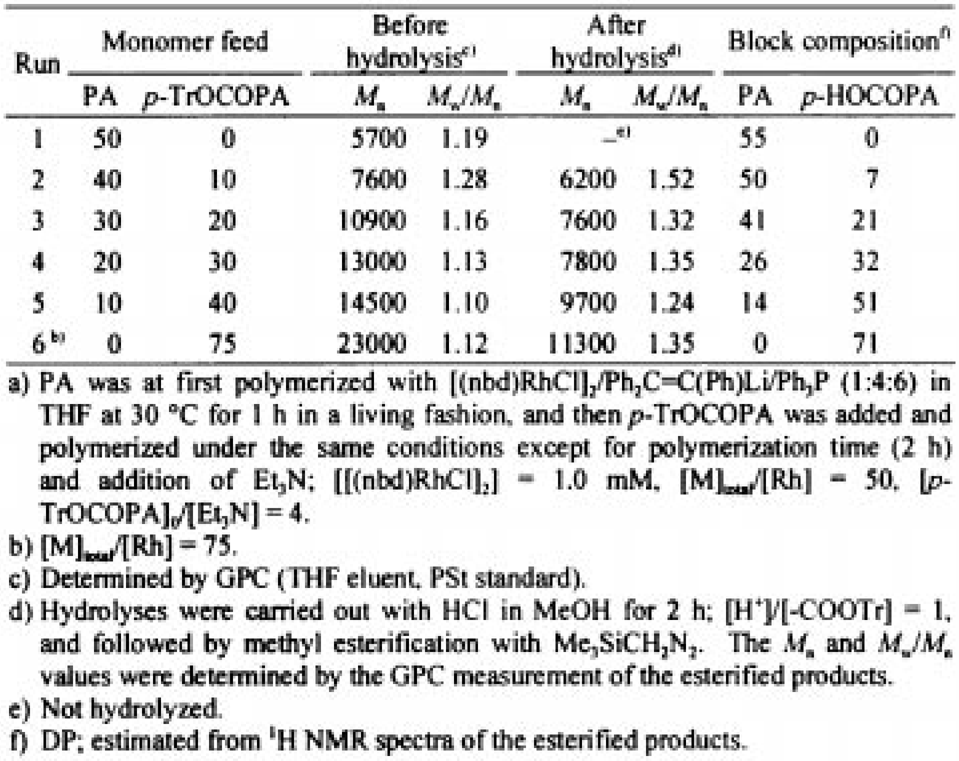
Run	Additive	[additive] / [-COOTr]	Reactn. time, h	Polymer after hydrolysis[b]		
				M_n	M_w/M_n	Ester convn., %[c]
1	None	–	20	9600	1.56	91.7
2	HCl *aq*	1	1	11300	1.35	98.5
3	AcOH *aq*	10	20	11400	1.51	93.0

a) *p*-TrOCOPA was polymerized with $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ (1:4:6) in THF at 30 °C for 2 h in a living fashion; $[[(nbd)RhCl]_2]$ = 1.0 mM, $[M]_0/[Rh]$ = 75, $[p\text{-TrOCOPA}]_0/[Et_3N]$ = 4. The estimated M_n and M_w/M_n values of poly(*p*-TrOCOPA) by GPC (PSt standard) were 23000 and 1.12, respectively.

b) Hydrolyses were carried out in MeOH and followed by methyl esterification with $Me_3SiCH_2N_2$. The M_n and M_w/M_n values were determined by the GPC measurement of the esterified products.

c) Estimated from ^1H NMR spectra of the hydrolyzed products.

Table 3. Hydrolysis of poly(PA)-*block*-poly(*p*-TrOCOPA) with various compositions[a)]



Run	Monomer feed		Before hydrolysis[c)]		After hydrolysis[d)]		Block composition[f)]	
	PA	*p*-TrOCOPA	M_n	M_w/M_n	M_n	M_w/M_n	PA	*p*-HOCOPA
1	50	0	5700	1.19	–[e)]		55	0
2	40	10	7600	1.28	6200	1.52	50	7
3	30	20	10900	1.16	7600	1.32	41	21
4	20	30	13000	1.13	7800	1.35	26	32
5	10	40	14500	1.10	9700	1.24	14	51
6[b)]	0	75	23000	1.12	11300	1.35	0	71

a) PA was at first polymerized with $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ (1:4:6) in THF at 30 °C for 1 h in a living fashion, and then *p*-TrOCOPA was added and polymerized under the same conditions except for polymerization time (2 h) and addition of Et_3N; $[[(nbd)RhCl]_2]$ = 1.0 mM, $[M]_{total}/[Rh]$ = 50, $[p\text{-TrOCOPA}]_0/[Et_3N]$ = 4.

b) $[M]_{total}/[Rh]$ = 75.

c) Determined by GPC (THF eluent, PSt standard).

d) Hydrolyses were carried out with HCl in MeOH for 2 h; $[H^+]/[\text{-COOTr}]$ = 1, and followed by methyl esterification with $Me_3SiCH_2N_2$. The M_n and M_w/M_n values were determined by the GPC measurement of the esterified products.

e) Not hydrolyzed.

f) DP; estimated from ^1H NMR spectra of the esterified products.

HOCOPA) hardly decreased and the PDI was kept relatively small. This indicates that the hydrolysis of trityloxycarbonyl group proceeds readily with hydrochloric acid. On the other hand, when acetic acid or no acid was added, about 90% of the ester group was hydrolyzed although it required longer reaction times (about 20 hours). In these cases, however, the DP_n of polymer more or less decreased and the PDI increased from 1.12 to *ca*. 1.5. These results indicate that degradation of polymer main chain occurs during a long reaction time. It was thus proved that poly(*p*-TrOCOPA) undergoes hydrolysis selectively when treated with hydrochloric acid in methanol.

Similarly, we examined the hydrolysis of poly(PA)-*block*-poly(*p*-TrOCOPA) with various block compositions by using hydrochloric acid (Table 3). Although the PDIs of the block copolymers somewhat increased, the DP_n values hardly decreased. These results show that hydrolysis of block copolymer also selectively occurs to introduce hydrophilic carboxyl groups in block copolymer.

Solubility of hydrolyzed block copolymers

The solubility properties of the hydrolyzed block copolymers were examined (Table 4). The solubilities of poly(PA) and poly(*p*-HOCOPA) homopolymers are also shown for comparison. Poly(PA) was soluble in many common organic solvents such as toluene, benzene, chloroform, and THF. Poly(*p*-HOCOPA) was soluble in DMSO, DMF, and basic water. The hydrolyzed block copolymers were soluble in DMSO and DMF irrespective of their block compositions and some of them were soluble in THF (PA:*p*-TrOCOPA = 50:7) or basic water (PA:*p*-TrOCOPA = 14:51). The solubility of

Table 4. Solubility properties of poly(PA)-*block*-poly(*p*-HOCOPA) with various compositions[a]

Solvent	PA : HOCOPA composition (DP)					
	55:0	50:7	41:21	26:32	14:51	0:71
hexane, Et_2O	×	×	×	×	×	×
toluene, benzene	○	□	×	×	×	×
$CHCl_3$, anisole	○	□	△	×	×	×
AcOEt	○	△	△	△	△	×
THF	○	○	□	□	△	×
PhCOOEt	○	○	□	□	□	×
DMSO, DMF	**○**	**○**	**○**	**○**	**○**	**○**
basic H_2O	×	×	×	△	○	○
MeOH	×	×	×	×	△	□
H_2O, acidic H_2O	×	×	×	×	×	×

a) ○: soluble, □: partly soluble, △: slightly soluble ×: insoluble.

these block copolymer was intermediate between those of poly(PA) and poly(*p*-HOCOPA) and depended on their block compositions.

Amphiphilic properties of hydrolyzed block copolymers

Amphiphilic properties of poly(PA)-*block*-poly(*p*-HOCOPA) were examined. At first, the micellization behavior of poly(PA)-*block*-poly(*p*-HOCOPA) was examined by ^{1}H NMR spectroscopy. Spectra of a hydrolyzed block copolymer in various solvents are shown in Figure 2. The copolymer showed all signals originating from both PA and *p*-HOCOPA units in the spectrum in DMSO-d_6. When the polarity of the solvent was lowered by the addition of benzene-d_6, signals a and b, which are assigned to *p*-HOCOPA, became smaller. In contrast, signal c due to the PA unit remarkably decreased when the polarity of the solvent was enhanced by the addition of deuterium oxide. These results clearly indicate that micelles with *p*-HOCOPA and PA cores have formed in nonpolar and polar solvents, respectively.

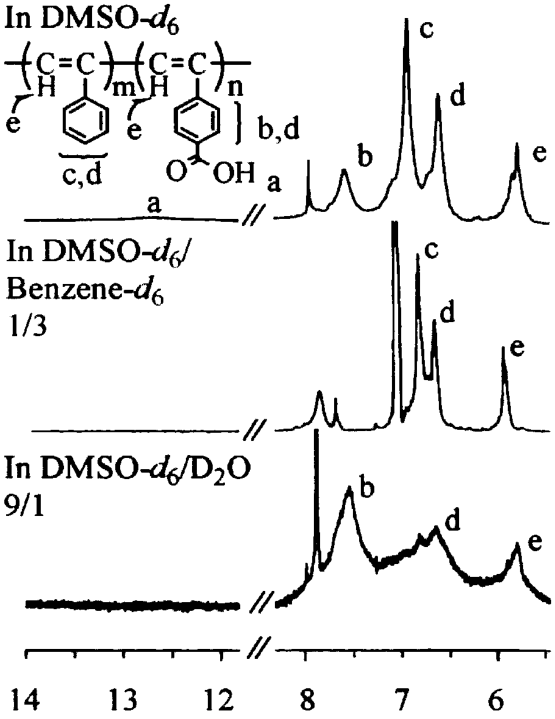


Figure 2. ^{1}H NMR spectra of poly(PA)-*block*-poly(HOCOPA) [block composition = 41:21] in various solvents.

Next, the formation of monomolecular membrane of poly(PA)-*block*-poly(*p*-HOCOPA) at the air-water interface was examined by the Langmuir-Blodgett technique. We used here the block copolymer whose block composition (DP ratio) was 50:7. The π-A profile is shown in Figure 3. This π-A plot was obtained reproducibly for several times of measurements. This result suggests that the block copolymer forms monomolecular membrane on the

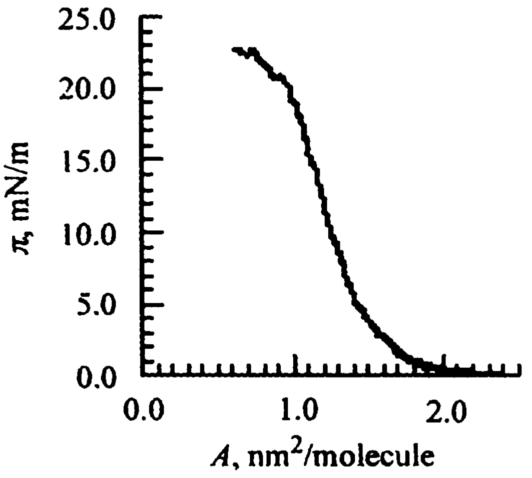


Figure 3. π-*A* plot of poly(PA)-*block*-poly(HOCOPA) [block composition = 50:7].

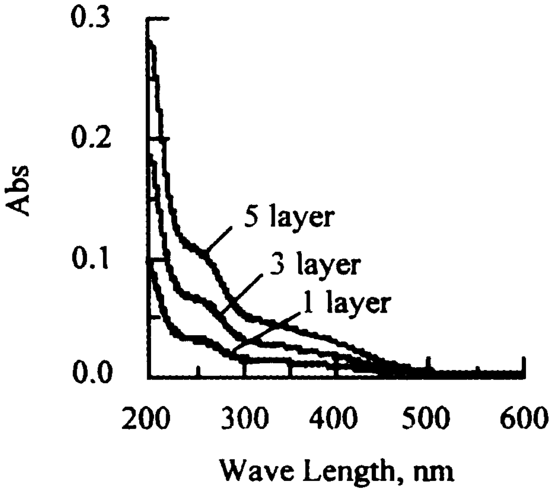


Figure 4. UV-visible spectra of LB membranes of poly(PA)-*block*-poly(HOCOPA) [block composition = 50:7].

water surface. This monomolecular membrane was accumulated on a quartz plate, and the UV-visible absorption spectra of accumulated membranes were measured (Figure 4). Clearly, the UV absorption band increases nearly in proportion to the number of accumulation. These results reveal that the hydrolyzed block copolymer forms monomolecular membrane on the water surface.

In summary, a new conjugated block copolymer, poly(PA)-*block*-poly(*p*-HOCOPA), has been successfully synthethzed. The ability of this block copolymer to form micelles and monomolecular membraane clearly demonstrates that it possesses the amphiphilic nature.

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