

## Novel synthetic methods of condensation polymers and their applications as new composite and opto-electronic materials

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**Abstract** - A direct polycondensation reaction, which is carried out by using phosphorylating agents such as triphenylphosphine as an initiator, was applied to the in-situ formation of various condensation polymers including high temperature polymers within various matrix polymers so that those rigid rod-like polymers were well dispersed within the matrix polymers. Improvements in tensile strength and modulus of the matrix polymers were achieved and new concept of molecular composite materials was established.

Ultra thin films of high temperature polymers such as poly(benzimidazole) (PBI) or poly(benzthiazole) (PBT) were successfully formed at air/water interface by using Langmuir-Blodgett method. Those ultra-thin films of high temperature polymers were quite stable up to 300°C and were highly insulative for electric current. They also exhibited interesting behaviors in terms of Non-Linear Optical properties.

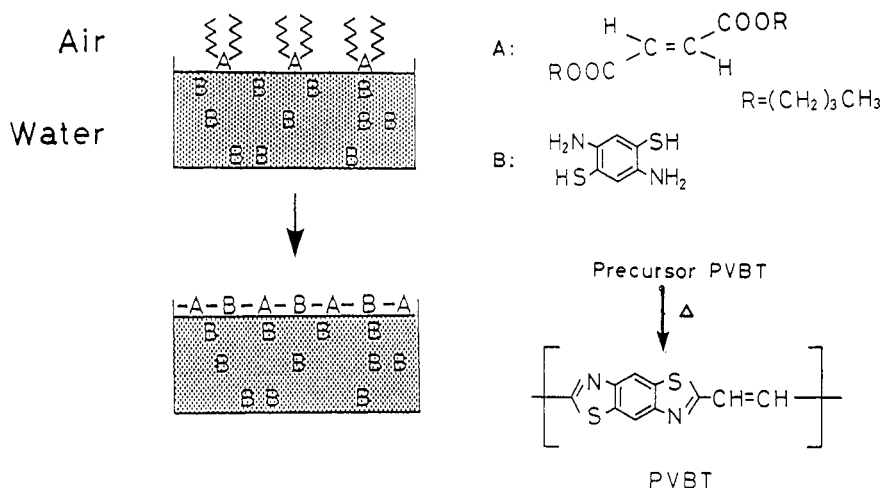
### INTRODUCTION

Condensation polymers such as polyamides or polyesters are usually crystalline and thermally stable, so that they are very much useful for the applications as structural materials such as fibers, films or composite materials. Conventional methods for preparing these condensation polymers are usually based on polycondensation reactions which are carried out at high temperatures above 250°C in order to eliminate leaving groups such as water out of the reaction phases. In order to carry out the polycondensation reactions under mild conditions, one needs a modification of functional groups to enhance the reactivity of functional groups in such ways as the modification of carboxylic acid to acid chloride. Interfacial or solution polycondensation methods are well-known to prepare high temperature polymers which can not be obtained by the melt polycondensation method.

Methods have been developed to prepare various condensation polymers by carrying out the polycondensation reactions without the modification of functional groups under mild conditions. Direct polycondensation reactions using various phosphorus compounds are an effective method for the synthesis of condensation polymers under mild conditions. For instance, triphenylphosphine (TPP) or triphenylphosphine dichloride (TPPCl<sub>2</sub>) can easily initiate the direct polycondensation in inert polar solvents such as N-methylpyrrolidone (NMP) or methylene chloride in the presence of bases such as pyridine or triethylamine. The direct polycondensation reactions are usually complete within half an hour at ambient temperature, with the precipitation of condensation polymers (ref. 1-3).

When monomers to prepare condensation polymers are dissolved in these inert polar solvents in which various polymers are dissolved together with these monomers, and the direct polycondensation method is applied to the solution, it is expected that an in-situ direct polycondensation of these monomers would take place in the polymer solutions into which resulting condensation polymers would be finely dispersed, possibly on a molecular basis. Usually, the compatibilities of condensation polymers with other polymers are so poor that blending of these two polymers causes phase separations by means of either melt or solution blending methods. This concept of the in-situ direct polycondensation in various matrix polymers may lead to a novel approach to molecular composites of the combination of various matrix polymers with condensation polymers, particularly liquid crystal polymers (LCP). The in-situ formation of LCPs in various matrix polymers may result in the improvement in mechanical properties at elevated temperatures so that a self-reinforcement effect of the matrix polymers is attained.

Aromatic polymers are known for their outstanding thermal stability, solvent resistance, and optical properties. However, they have severe processing problems due to the lack of soluble and processable polymers. Particularly, opto-electronic applications of polymers request ultra-thin films with highly oriented structures. Recent developments for the requirements have been focused on the synthesis of ultra-thin films of various polymers by means of Langmuir-Blodgett (LB) technique. It was found previously that amphiphilic Schiff bases derived from terephthalaldehyde reacted easily with aromatic diamines at air/water interface when they were spread on water containing these aromatic diamines and thus, high temperature polymers such as poly(benzimidazole) (PBI), poly(benzoxazole) (PBO), or poly(benzthazole) (PBT) were obtained in forms of ultra-thin films with multi-layers (ref. 4-6). An example to prepare poly(vinylenebenz thiale) (PVBT) to form thin films at air/water interface can be illustrated as follows:



It is expected that these ultra-thin films of high temperature polymers would exhibit opto-electronic activities such as Non-linear optics (NLO) since they consist of fully conjugated chains with highly polar groups.

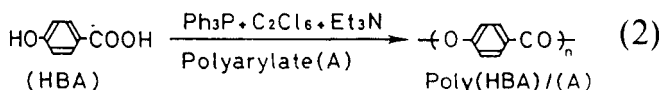
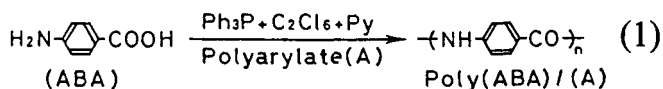
This paper describes novel synthetic methods of condensation polymers in terms of two points of views. One is the novel molecular composites by means of *in-situ* direct polycondensation and the other is the formation of ultra-thin films of high temperature polymers at air/water interface, which are applied to opto-electronics in terms of NLO.

### **IN SITU DIRECT POLYCONDENSATION: APPROACHES TO MOLECULAR COMPOSITES**

Typical examples of the *in-situ* polycondensation were carried out as follows: polyarylate (A) [copolyester from tere-/iso-phthalic acids (1/1) and bisphenol A] 5.75 g and p-aminobenzoic acid (ABA) 2.745 g ( $2 \times 10^{-2}$  mol) were dissolved in a mixed solvent of 80 cm<sup>3</sup> methylene chloride and 10 cm<sup>3</sup> pyridine, into which 6.3 g ( $2.4 \times 10^{-2}$  mol) of triphenylphosphine (TPP) were dissolved to make a clear solution. After complete dissolution, 7.1 g ( $3.0 \times 10^{-2}$  mol) of hexachloroethane were added to the solution all at once with vigorous stirring. The reaction took place immediately and the entire solution was kept at 25°C for 24 h. The initial clear solution turned to a thick milky suspension owing to the formation of poly(ABA) in the solution of polyarylate. However, no macroscopic phase-separation occurred in the suspension even after standing the suspension for more than two weeks. The resulting poly(ABA) was so well-dispersed in the solution that no precipitation of the coagulate took place.

The *in-situ* direct polycondensation of p-hydroxybenzoic acid (HBA) in polyarylate solution was carried out as follows: 5.77 g of polyarylate and 2.762 g ( $2 \times 10^{-2}$  mol) of HBA were dissolved in 250 cm<sup>3</sup> of 1,1,2,2-tetrachloroethane, followed by complete dissolution of 5.508 g ( $2.1 \times 10^{-2}$  mol) of TPP. To the solution was added 5.681 g ( $2.4 \times 10^{-2}$  mol) of hexachloroethane and the solution was heated to 100°C for complete dissolution, followed by cooling down to 25°C. A portion of 5.6 cm<sup>3</sup> ( $0.4 \times 10^{-2}$  mol) of triethylamine was added to the solution to initiate the *in-situ* direct polycondensation.

The obtained suspension of poly(HBA) was quite stable and no macroscopic phase-separation took place. The reaction schemes are shown as follows:



The obtained suspensions were poured into excess methanol and the polymers were collected by filtration, followed by repeated extractions with hot methanol to eliminate monomers and by-products such as triphenylphosphine oxide (TPPO) formed by the direct polycondensation. The extracted polymers were dried under vacuum and redissolved in methylene chloride. Films were obtained by casting the solution on a glass plate.

Fig. 1 indicates infra-red spectra of the films which suggest the existence of poly(ABA) or poly(HBA) in polyarylate.

Fig. 2 shows viscoelastic properties of the films of polyarylate containing poly(ABA) or poly(HBA) in terms of the storage modulus ( $G'$ ) and the loss tangent ( $\tan \delta$ ) of the films. It is seen in Fig. 2 that polyarylate A shows a main relaxation owing to  $T_g$  at  $187^\circ\text{C}$  with an auxiliary peak at  $110^\circ\text{C}$ . The main relaxation of A-a and A-e did not significantly change, while no auxiliary peak appeared at around  $110^\circ\text{C}$  for both A-a and A-e. The existence of rigid rod-like poly(ABA) or poly(HBA) within the matrix of A might prevent the movement of the main chains of polyarylate so that the auxiliary peak at  $110^\circ\text{C}$  owing to side chain motions of isopropane units of bisphenol A might disappear.

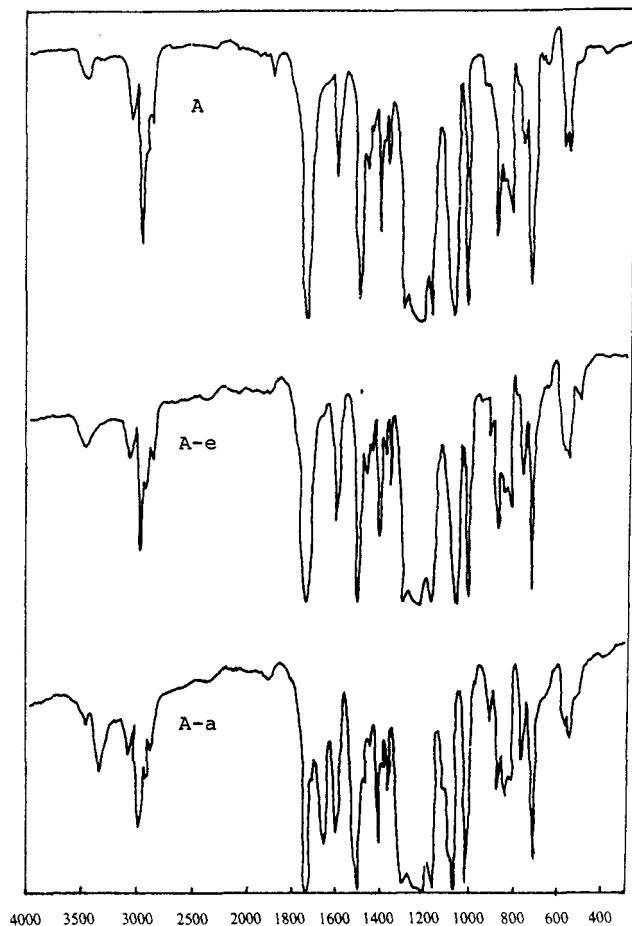


Figure 1 Infrared spectra of the films.  
A, polyarylate;  
A-e, polyarylate containing 21 wt% of poly(HBA);  
A-a, polyarylate containing 29 wt% of poly(ABA).

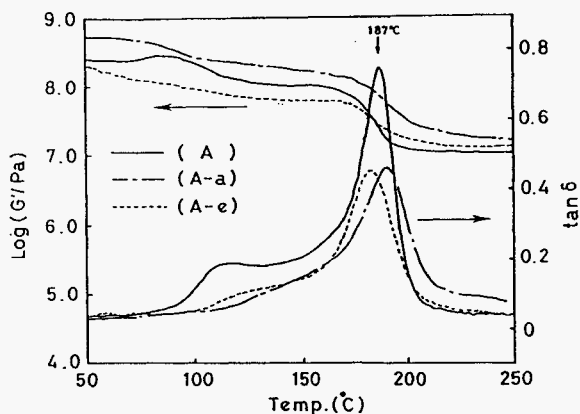


Figure 2 Temperature dependences of  $G'$  and  $\tan \delta$  measured at 1 Hz. A, polyarylate; A-a, polyarylate containing 29 wt% of poly(ABA); A-e, polyarylate containing 21 wt% of poly(HBA).

Table I Mechanical properties of films at various temperatures

Sample	Temp. °C	Tensile strength	Tensile modulus
		MPa	MPa
A	23	41	1800
	100	20	980
	150	7.3	270
A-e	23	33	2100
	100	21	1300
	150	6.0	400
A-a	23	30	2100
	100	20	1300
	150	13	1100

A, polyarylate; A-e, polyarylate containing 21 wt% of poly(HBA); A-a, polyarylate containing 29 wt% of poly(ABA).

Table I summarizes mechanical properties of A, A-a, and A-e at various temperatures, for tensile strength and modulus. Tensile strength dropped at 23°C from 41 MPa to 30-33 MPa in the presence of rigid poly(ABA) or poly(HBA), while the modulus of the films increased from 1800 MPa to 2100 MPa, a 17% increase. The tensile strength of polyarylate A decreased remarkably with increasing temperature up to 150°C from 41 MPa to 7.3 MPa. On the other hand, A-a which contained 29 wt% of poly(ABA), maintained the high tensile strength at 150°C, presumably owing to the self-reinforcement effect of the rigid rod-like polymers which were well dispersed within the matrix polymer A. In particular, the modulus of A-a and A-e was in the range of 400 and 1100 MPa at 150°C. These results show that the mechanical properties of polyarylate were greatly improved by the formation of poly(ABA) or poly(HBA) within polyarylate.

Fig. 3 shows cross-sections of the films of A-a and A-e, which were observed under a cross-polarized microscope. As seen in Fig. 3, poly(ABA) in polyarylate had an aggregated form, like chains, while poly(HBA) was well-dispersed in polyarylate in a fine particle form with a diameter of about 0.01  $\mu$ m. Since polyamides form strong hydrogen bonding among chains, the aggregation tendency of poly(ABA) might be stronger than that of poly(HBA). Moreover, the affinity of poly(HBA) to polyarylate may be better than poly(ABA) since they belong to the same family of polyesters. These dispersion states of rigid rod-like polymers may reflect the difference in the mechanical properties of A-a and A-e.

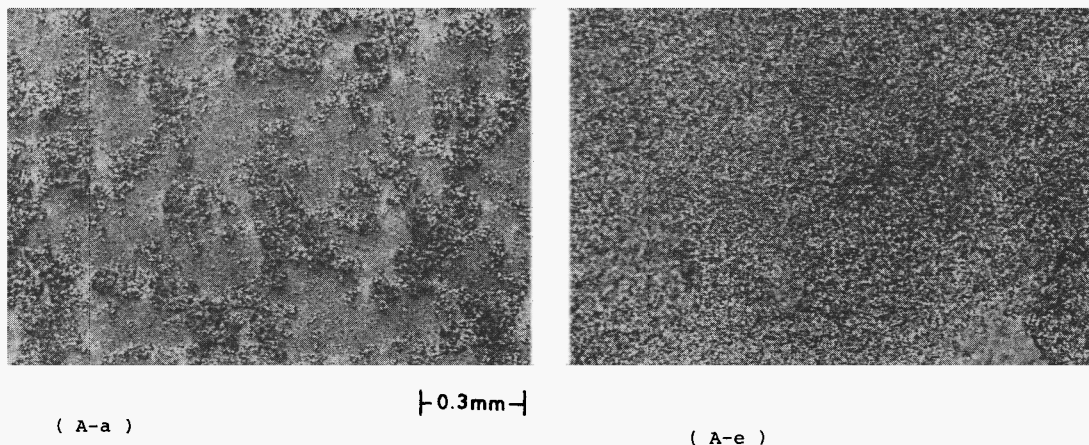
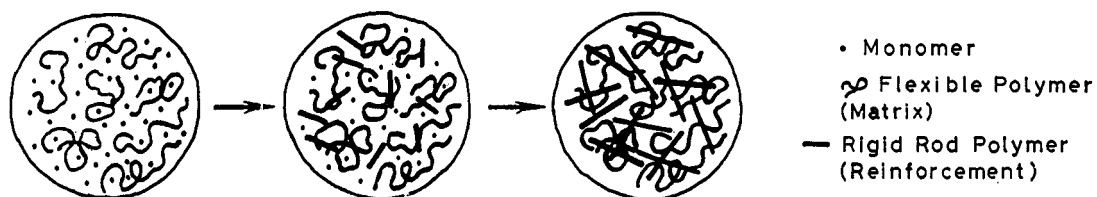
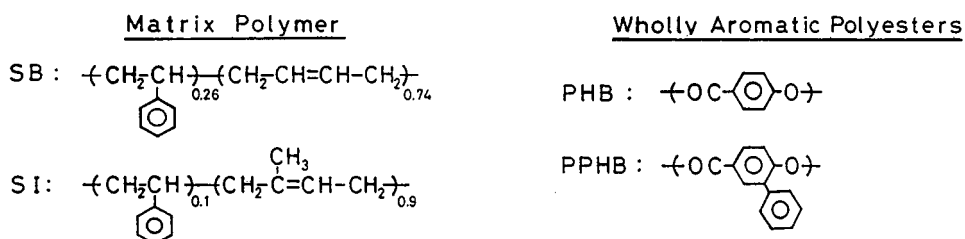


Figure 3 Cross-polarized microscopic pictures of cross-sections of the films. A-a, polyarylate containing 29 wt% of poly(ABA); A-e, polyarylate containing 21 wt% of poly(HBA).

When a flexible polymer such as rubber is used as a matrix polymer, the self-reinforcing effect of the *in-situ* formed LCP's would be more eminently observed. Moreover, the compatibility of rubber and LCP's is so poor that phase-separations occur by blending, in fact, blending is almost impossible between rubber and LCP's. Therefore, the *in-situ* direct polycondensation would provide only a chance to make blend polymers of rubber and LCP's, as can be illustrated as follows:



The *in-situ* direct polycondensation of HBA or 3-phenyl-4-hydroxybenzoic acid (PHBA) was carried out in solutions of rubbers derived from styrene/butadiene (SB) or isoprene (SI), which were used as matrix polymers. Chemical compositions of SB and SI, and LCP's are shown as follows:



The *in-situ* direct polycondensation in rubber solutions was carried out in the same manner as that in polyarylate solutions. Table II summarizes results of the *in-situ* direct polycondensation in SB or SI solutions at various feed ratios of HBA or PHBA. The content of poly(HBA) (PHB) or poly(PHBA) (PPHB) was measured by elemental analyses of resulting polymers. When the content of PHB or PPHB was as low as 7 mol%, the reaction phases were apparently homogeneous.

Viscoelastic properties of the films containing PHB or PPHB were measured in terms of  $G'$  and  $\tan \delta$ . Results are summarized in Fig. 4, as temperature dependences of  $G'$  and  $\tan \delta$ . In case of SB,  $T_g$  at  $-97^\circ\text{C}$  of SB units shifted toward higher temperatures up to  $-90^\circ\text{C}$  for SB/PHB-1 and  $-81^\circ\text{C}$  for SB/PPHB. Particularly,  $T_g$  peak at  $60^\circ\text{C}$  owing to block units of styrene disappeared completely for SB/PPHB, while the peak was observed for SB/PHB. On the other hand,  $T_g$  at  $-68^\circ\text{C}$  of SI shifted slightly to  $-65^\circ\text{C}$  for SI/PPHB-1 and no significant changes in spectra of  $G'$  and  $\tan \delta$  were observed.

Table.II Synthesis of Composite Polymers.

Code	PHB or PPHB Content (mol%)		Yield (%)	Reaction Phase
	Monomer	Film a)		
SB/PHB-1	12	7.3	79.0	homo.
SB/PHB-2	28		64.8	hetero.
SB/PPHB-1	12	11.3	79.3	homo.
SB/PPHB-2	28		98.0	hetero.
SI/PHB-1	12	7.1	84.7	homo.
SI/PHB-2	29		83.0	hetero.
SI/PPHB-1	12	10.9	92.8	homo.
SI/PPHB-2	29		99.6	hetero.

a) Measured by elemental analysis.

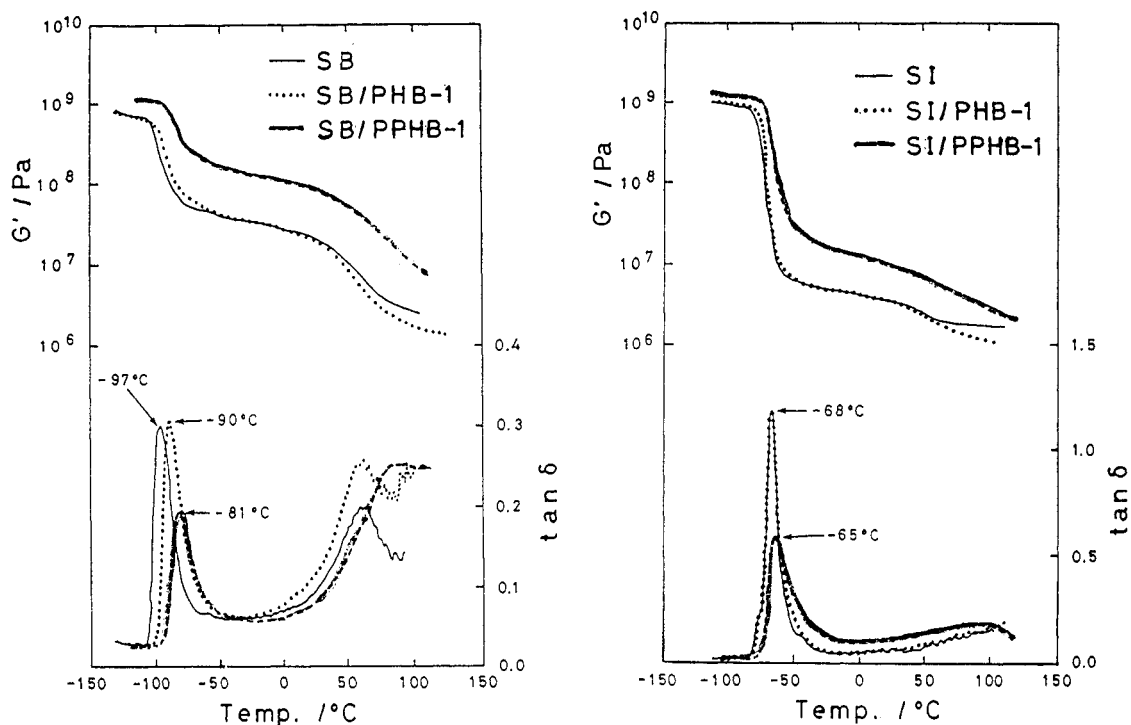


Fig. 4 Temperature dependences of  $G'$  and  $\tan \delta$  of the films

These results on viscoelastic properties of the films implies a strong interaction of phenyl substituent of PPHB with styrene units of SB. Photomicrographs of the cross-section of the films indicated that the dispersed state of PPHB in either SB or SI was more homogeneous than the case of PHB. Therefore, PPHB formed *in-situ* in SB or SI had better affinity with SB or SI owing to the strong interaction of phenyl substituent of PPHB with styrene units of SB or SI.

Mechanical properties of the films containing PHB or PPHB in SB or SI were measured at various temperatures and results are summarized in Table III. Yield stress and modulus of the films were greatly improved by the incorporation of rigid rod-like PHB or PPHB in SB or SI, and the mechanical improvements became more prominent at higher temperatures such as 70°C. The

Table III Mechanical properties of films containing LCP

Temp	Items	SB	SB/ PHB-1	SB/ PPHB-1	SI	SI/ PHB-1	SI/ PPHB-1
23°C	Yield Stress (k g/cm <sup>2</sup> )	24	28				
	Ulti. Stress (k g/cm <sup>2</sup> )	76	100	63	*	18	10
	Modulus (k g/cm <sup>2</sup> )	665	957	2180	21	16	152
	Elongation (%)	640	693	440	1600以上	1070	180
50°C	Yield stress (k g/cm <sup>2</sup> )	14	18	40	5		
	Ulti. Stress (k g/cm <sup>2</sup> )	13	14	29	5	5	6
	Modulus (k g/cm <sup>2</sup> )	289	450	1210	8	10	56
	Elongation (%)	411	370	77	582	657	66
70°C	Yield Stress (k g/cm <sup>2</sup> )	7	9	23	2	2	
	Ulti. Stress (k g/cm <sup>2</sup> )	3	6	17	1	1	3
	Modulus (k g/cm <sup>2</sup> )	79	166	740	5	8	34
	Elongation (%)	220	111	31	328	510	80

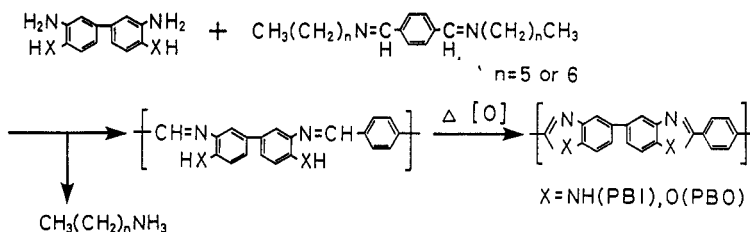
incorporation of PPHB in SB or SI resulted much better improvements of the mechanical properties in terms of yield stress and modulus, as can be seen in Table III. The enhancement effect of PPHB in SB or SI may also be due to the strong interaction of the phenyl substituent of PPHB with styrene units of SB or SI, which was suggested by the viscoelastic properties of the films.

The *in-situ* direct polycondensation of monomers which form rigid rod-like LCP's leads to improve mechanical properties of matrix polymers, particularly at elevated temperatures, owing to the self-reinforcement of the rigid LCP's and a novel type of "molecular composites" is derived by this method.

### ULTRA-THIN FILMS OF HIGH TEMPERATURE POLYMERS FOR OPTO-ELECTRONIC APPLICATIONS: NEW NLO POLYMERS

Thin films of polymers have been focused in terms of electronic or opto-electronic applications. For these applications, highly oriented structures of the thin films are required to attain more sophisticated properties on molecular bases. In order to achieve the requirement, LB technique can provide a good molecular orientation of amphiphilic molecules such as stearic acid on water surface. However, mechanical properties of the LB films are not satisfactory since the line-up molecules are independent without having covalent bonds. It is known to make mono-layer films by using amphiphilic polymers, but their thermal stability is not so high owing to the presence of long aliphatic groups.

It was found previously (ref. 4-6) that ultra-thin films of high temperature polymers could be formed at air/water interface and the built-up films could be transferred onto quartz substrates as multi-layer films. The formation of the built-up films could be carried out by reacting amphiphilic Schiff base derived from terephthalaldehyde which was spread on water containing diamine derivatives. The reaction scheme is shown as follows:



Thus, poly(benzimidazole) (PBI) or poly(benzoxazole) (PBO) were formed at air/water interface as ultra-thin films which could be transferred onto various substrates such as quartz or calcium fluoride. Fig. 5 shows the film thickness as functions of number of layers deposited onto  $\text{CaF}_2$ . Per layer thickness of the built-up films of the precursor polymer to PBO was  $36 \text{ \AA}$ , while that of PBO obtained by the thermal conversion was  $30 \text{ \AA}$ .

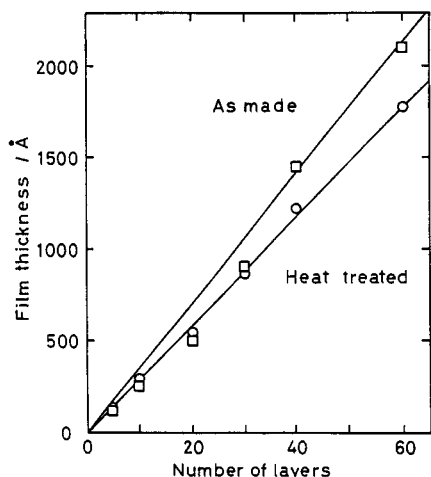


Fig. 5 Thickness of the films as functions of number of layers

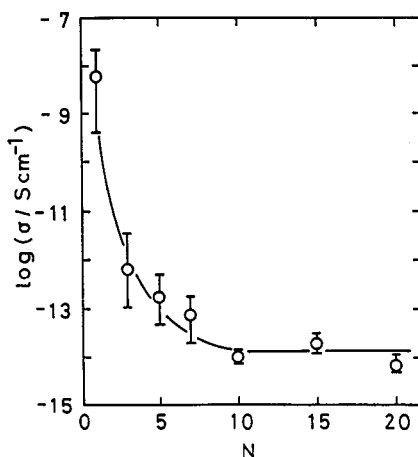


Fig. 6 Electric conductivities of the PBO thin films as functions of number of layers at room temperature - Al/PBO/Al

Fig. 6 indicates electric conductivities of the PBO thin films as functions of number of layers. The conductivity of one layer film of PBO was about  $10^{-8}$  S/cm, and it decreased with increasing number of layers of the films. The conductivity of the built-up films reached  $10^{-14}$  S/cm for the films of more than 6 layers, which was equal to the conductivity of the PBO film obtained by solvent casting. Fig. 7 shows temperature dependences of the conductivity of the PBO thin films with different number of layers. The PBO thin film of one layer indicated a tunneling current through the thin film.

The thin films of PBO were found to be a good insulator when more than 10 layers were deposited onto substrates. The thin films of PBO were very stable up to temperatures of  $300^{\circ}\text{C}$  and they started to degrade above  $400^{\circ}\text{C}$ . Mechanical properties of the thin films of PBO were tough and no scratch was formed on the surface by finger.

Fig. 8 indicates the relationship between current (I) and voltage (V) of the multi-layers films of PBO. The thin films of less than  $N=3$  indicated the current response deviated from the ohmic behavior at low voltages and increased exponentially with voltages, presumably owing to the tunneling conduction through the films. On the other hand, the multi-layers films of more than  $N=5$  indicated an ohmic current response up to 0.7 V and the current increased at high voltages, indicating that the multi-layers films of PBO have a good insulating property.

Schiff base derived from terephthalaldehyde was subjected to the reaction with 2,5-diamino-1,4-dimercaptobenzene at air/water interface by means of the same procedure as the case of PBI or PBO. The reaction mechanism was slightly different from that of the formations of PBI or PBO. The reaction proceeded through the addition reaction of mercapto groups to the Schiff base, followed by the elimination of alkylamine as shown in following scheme:

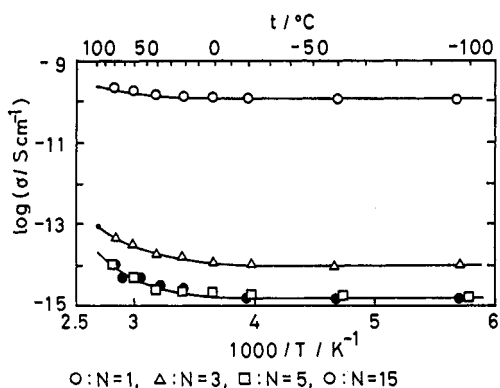
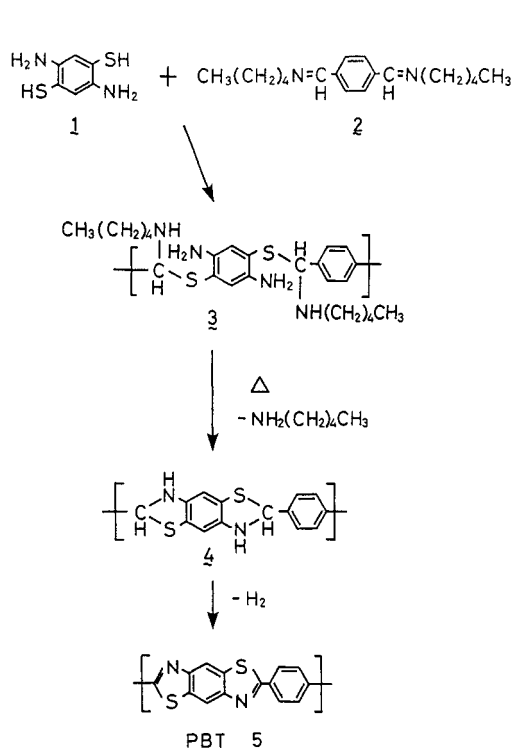


Fig. 7 Electric conductivities of the PBO thin films at various temperatures - Al/PBO/Al

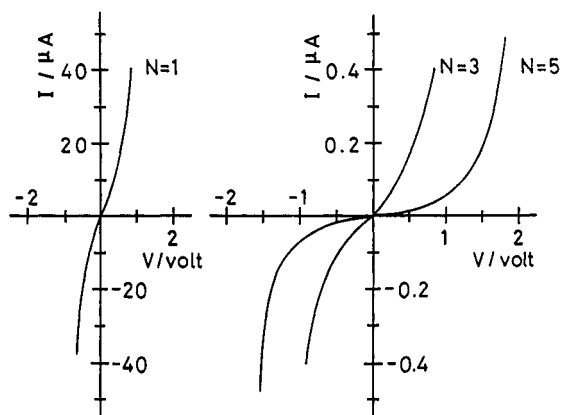
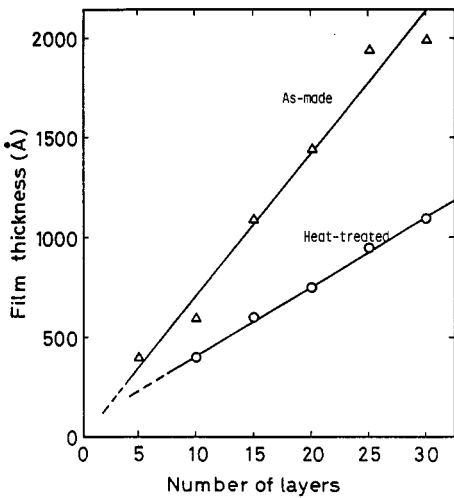


Fig. 8 V-I curves of the multi-layers thin films of PBO





Substrate	Film	$\chi^3$ value ( $\times 10^{12}$ esu)
quartz	PBO	1.85
quartz	PBI	6.00
CaF <sub>2</sub>	PBT (as made)	6.00
CaF <sub>2</sub>	PBT (heat-treat)	9.56

Fig. 9 Thickness of built-up films as made and after heating (300°C, 30 min) as a function of number of layers (N)

Poly(benzthiazole) (PBT 5) was obtained as built-up thin films, which were heat-treated at temperatures above 300°C for the ring-closure reaction. Fig. 9 indicates the thickness of the thin films as made and after heat-treatment at 300°C as a function of number of layers. Per layer thickness of the as-made film was 71 Å, while that of the heat-treated film was 35 Å. The big difference in the film thickness is presumably due to the elimination of pentylamine by the heat treatment.

Electric properties of the thin films of PBO were almost similar with those of PBI or PBO and they were insulative with the conductivity of  $10^{-15}$  S/cm when the multi-layers were above 5 layers, and a tunneling current was observed for the one layer film of PBT.

Since PBI, PBO or PBT are fully conjugated polymers containing hetero atoms such as nitrogen or sulfur, it is highly expected that those ultra-thin films of PBI, PBO, or PBT would exhibit interesting opto-electronic properties such as non-linear optics (NLO). Third harmonic generation (THG) was measured for the thin films (10 layers) of PBT as shown in Fig. 10, which indicates a marker fringe pattern.

THG values for the thin films of these high temperature polymers were estimated as shown in Table IV. PBT thin film had the highest THG value among those high temperature polymers.

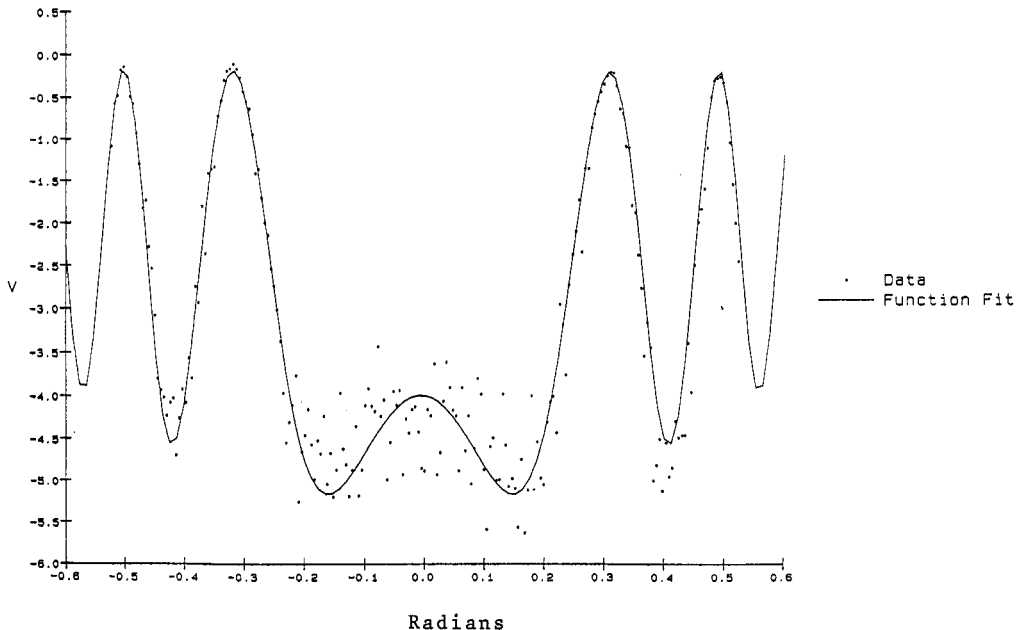


Fig. 10 Marker fringe pattern of THG for the thin film (350 Å) of PBT

Second harmonic generation (SHG) requires highly polar structures with a good molecular orientation, in other words, a molecular architecture is required in terms of non-centrosymmetric structures having electron-donating and -accepting groups. Therefore, an electron-accepting nitro group was tried to introduce into the PBT as described in following scheme:

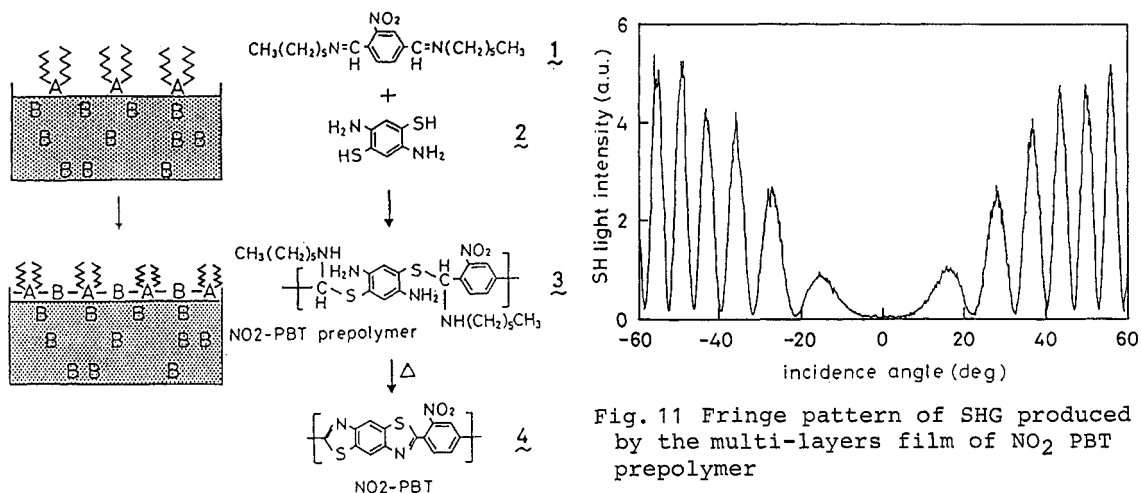


Fig. 11 Fringe pattern of SHG produced by the multi-layers film of NO<sub>2</sub> PBT prepolymer

2-nitro-dihexylterephthalaldimine 1 was obtained by the nitration of terephthaldehyde, followed by the reaction with n-hexylamine. The method to prepare the PBT containing nitro group was the same as PBT. It was abbreviated as NO<sub>2</sub>-PBT.

The NO<sub>2</sub> PBT precursor polymer could not be deposited onto a glass substrate by a vertical lifting method of LB technique by means of conventional LB trough because of the friction between the film on water surface and the wall of the LB trough. Therefore, a moving-wall type trough was applied to lift the thin film formed at air/water interface and the film of the NO<sub>2</sub> PBT prepolymer could be deposited as Z-type deposition with the deposition ratio of 1. It is very important for the film to have the Z-type deposition since the non-centrosymmetric structure is absolutely necessary for the SHG activity.

Fig. 11 indicates results of the SHG activity of the prepolymer of NO<sub>2</sub> PBT, which exhibited a clear marker fringe pattern with the incidence angle of laser beam. Therefore, the multi-layers film of the NO<sub>2</sub> PBT prepolymer has a good orientation of molecular chains on the surface of the substrate with a constant angle.

The thin films of the NO<sub>2</sub> PBT prepolymer was heat-treated at 300°C so that it was converted to the PBT structure. After the heat-treatment, the SHG activity of the thin film of NO<sub>2</sub> PBT was measured. The intensity of the SHG activity decreased to one fourth of the prepolymer. The decrease of the SHG activity might be caused by the disorder of the molecular orientation on the substrate. However, thermal stability of the prepolymer of the NO<sub>2</sub> PBT would be sufficiently high enough toward the irradiation of high energy laser beam and the practical application of those thin films for NLO would be highly possible.

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